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Mixed Self-Assembled Monolayer Gate Dielectrics for Continuous Threshold Voltage Control in Organic Transistors and Circuits

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Organic thin-film transistors (TFTs) are potentially useful for flexible displays,[1] conformable sensor arrays,[2] and analog or digital integrated circuits.[3,4] Especially for digital circuits it is important that the threshold voltage of the transistors can be set to a specific value during transistor fabrication. The reason is that the threshold voltage of the transistors determines the input voltage at which the circuits switch between the two logic states ("0" and "1").[5,6] Ideally, this switching voltage is exactly half the circuit's supply voltage, since this provides the maximum voltage difference between the switching voltage and both the ground potential and the supply voltage potential, which in turn provides the maximum immunity of the circuits against the influence of electrical noise that is always present in electronic systems.[5,6] If the threshold voltage of the transistors cannot be controlled during manufacturing, the switching voltage may be too close to either the ground potential or the supply voltage potential, in which case the circuits may not work reliably (i.e., switch inadvertently) when exposed to electrical noise. Therefore, it is highly desirable that the threshold voltage of the transistors can be set to a specific value determined by the circuit designer.

Previously described methods to control the threshold voltage of organic TFTs include the use of a corona discharge, a low-energy electron beam, or a large electric field to change the amount of charge or polarization within the polymer gate dielectric layer,[7–10] the use of ultraviolet radiation to change the electronic properties of the semiconductor/dielectric interface,[11] and the functionalization of the SiO_2 gate dielectric with a self–assembled monolayer (SAM) of a silane with more or less electronegative substituents.[12,13] Here we demonstrate a novel approach that allows the threshold voltage of low–voltage (≤3 V) organic p-channel and n-channel TFTs and the switching voltage and noise margin of low-power organic complementary circuits to be tuned continuously over a wide range during manufacturing. Continuous threshold voltage tuning is facilitated by employing gate dielectrics that are based on mixed alkyl/fluoroalkyl phosphonic acid SAMs prepared by a simple solution process. The threshold voltage of the TFTs is a linear function of the atomic fluorine concentration in the mixed SAM dielectric, with a modulation coefficient of 40 mV/%.

The transistors and circuits are fabricated on glass substrates (see **Figure 1a**). Patterned gate electrodes are defined by depositing 30 nm thick aluminum by vacuum evaporation through a shadow mask, followed by a brief oxygen plasma that increases the thickness of the native aluminum oxide (AlO_x) layer from ~1.5 nm to 3.6 nm. The substrate is then immersed in a mixture of octadecylphosphonic acid (Figure 1b) and 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentadecylfluoro-octadecylphosphonic acid (Figure 1c) in 2-propanol, allowing a mixed organic monolayer to self-assemble on the oxidized aluminum. The total thickness of the AlO_x/SAM gate dielectric is 5.7 nm.[14–18] The conjugated organic semiconductors pentacene (for p-channel TFTs) and hexadecafluorocopperphthalocyanine ($F_{16}CuPc$, for n-channel TFTs) are then deposited in vacuum through shadow masks. TFTs and circuits are completed by evaporating gold source/drain contacts through another shadow mask. The highest process temperature is 90 °C (the substrate temperature during the $F_{16}CuPc$ deposition), which is fully compatible with flexible polymeric substrates.[14] All electrical measurements are performed at room temperature in air.

Compared with alkyl SAMs, the electronegative substituents in fluoroalkyl SAMs reduce the electron density in the carrier channel of the transistors, causing a change in threshold voltage towards more positive values. This was first demonstrated by Kobayashi et al. and Pernstich et al. for organic TFTs prepared on silicon substrates with thick, thermally grown SiO_2 gate dielectrics functionalized with various silane SAMs.[12,13] Kobayashi and Pernstich showed that the threshold voltage changes by a certain amount when the SiO_2 is covered with a SAM of a fluoroalkyl silane, rather than an alkyl silane. In contrast to the single-component SAMs employed by Kobayashi and Pernstich, we have prepared mixed SAMs of alkyl and fluoroalkyl molecules in order to tune the threshold voltage continuously, rather than discretely, by adjusting the mixing ratio of the two molecules. Having continuous control over the threshold voltage

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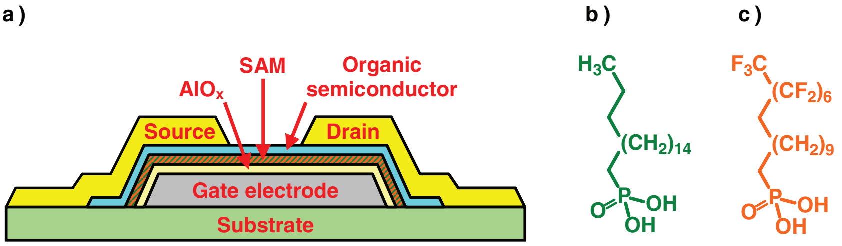

Figure 1. a) Schematic cross-section of the thin–film transistor (TFT) structure. The gate dielectric is a combination of a 3.6 nm thick, plasma-grown aluminum oxide layer and a 2.1 nm thick alkyl/fluoroalkyl phosphonic acid self-assembled monolayer. b) Chemical structure of octadecylphosphonic acid. c) Chemical structure of pentadecylfluoro–octadecylphosphonic acid.

makes it possible to place the switching voltage of the circuits at precisely half the supply voltage, producing the maximum noise margin. While Kobayashi and Pernstich employed silanes to form SAMs on high-temperature-grown SiO_2 dielectrics, we have utilized phosphonic acids to form high-quality monolayers on patterned Al gates covered with a thin AlO_x layer grown at room temperature.

Mixed SAMs have been studied by the Whitesides group[19] and by the groups of Allara and Weiss.[20] Bain et al. demonstrated that mixed SAMs are easily prepared by co-adsorbing aliphatic molecules with different tail groups from a mixed solution.[19] When Bain et al. compared the composition of the mixed SAMs (inferred from X-ray photoelectron spectroscopy (XPS) measurements) to the relative concentrations of the molecules in the adsorption solution they found that generally the ratio of the concentrations of the two components in the SAM is not the same as in solution, "but reflects the relative solubilities of the components in solution and interactions between the tail groups in the monolayers."[19] Interestingly, for a two-component system of methyl- and halogen-terminated thiols with the same chain length Bain et al. observed a linear relationship between the concentration in solution and the composition of the SAM.[19] This implies that the composition of mixed alkyl/fluoroalkyl SAMs can be tuned in a deterministic manner by adjusting the mixing ratio in the solution, as long as the alkyl and fluoroalkyl components have the same chain length. Therefore, both the alkyl and fluoroalkyl molecules utilized in this work have the same chain length (18 carbon atoms). In principle, chain lengths shorter than 18 carbon atoms are also possible, although the gate leakage currents tend to be larger for shorter chain lengths.[16,17]

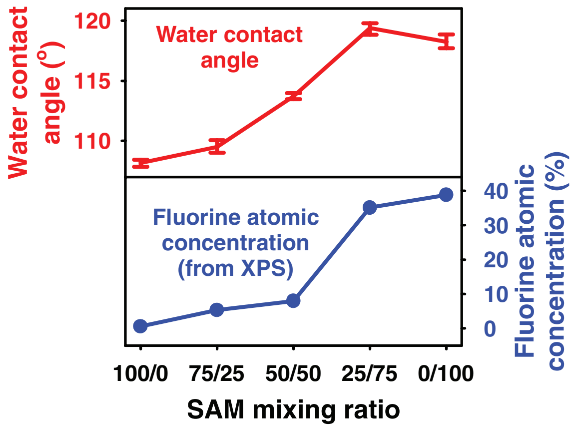

Figure 2. Relationship between the mixing ratio of alkyl and fluoroalkyl phosphonic acid molecules in the adsorption solution during SAM formation and the water contact angle (measured on the surface of the SAMs) and the atomic concentration of fluorine in the SAM-based gate dielectric (measured by X-ray photoelectron spectroscopy, XPS).

From contact-angle analysis Bain et al. further concluded that "multicomponent monolayers do not segregate into discrete single-component domains. Any islands that do form are too small to influence the contact angle by distorting the drop edge, placing an upper bound of about 0.1 µm on the size of any such islands."[19] This result was later challenged by Stranick et al. who investigated the structure of mixed SAMs with nanometer resolution by scanning tunneling microscopy (STM). They discovered that the molecules systematically phase separate into discrete domains.[20] However, the size of the molecular domains was less than 10 nm, i.e., several orders of magnitude smaller than the dimensions of thin-film transistors (usually >1 µm). This suggests that mixed SAMs lead to an effective electrostatic potential and that the impact of the different SAM molecules on the electron density in the semiconductor averages across the transistor dimensions, giving a uniform, reproducible effect on the threshold voltage.

We have measured water contact angles of 108° on octadecylphosphonic acid SAMs and 118° on pentadecylfluorooctadecylphosphonic acid SAMs. For mixed SAMs, contact angles between 108° and 118° would therefore be expected. Indeed, SAMs prepared from a solution containing equal amounts of alkyl and fluoroalkyl phosphonic acid gave a contact angle of 114° (see **Figure 2** and **Figure 3a–c**). Water contact angles measured on the same monolayer vary by less than 1° (see Figure S1, Supporting Information), indicating that the phase separation of the alkyl and fluoroalkyl molecules in the SAMs averages over microscopic areas, as suggested by Bain et al.[19] The SAM composition has no detectable systematic effect on the dielectric capacitance and on the leakage current density measured on Al/AlO_x/SAM/Au capacitors (see Figure S2, Supporting Information), confirming the high quality of the SAMs regardless of SAM composition. Analysis of the contact angles measured with water and with a non-polar liquid (n-heptane) using the Owen–Wendt method[21] shows that the surface energy of the SAM decreases from 20 mN/m to 12 mN/m as the fluoroalkyl content is increased from 0% to 100% (see Figure S3, Supporting Information).

The relationship between the mixing ratio in solution and the SAM composition is not linear. XPS measurements indicate that the concentration of fluoroalkyl phosphonic acid in the SAM approaches 100% even if the adsorption solution contains only 75% fluoroalkyl phosphonic acid (see Figure 2). This suggests that the adsorption of the fluoroalkyl phosphonic acid is favored over that of the alkyl phosphonic acid when the fluoroalkyl content in the solution exceeds 50%.

Figure 3d–f show the transfer characteristics of pentacene p-channel and F_{16}CuPc n-channel TFTs prepared with gate

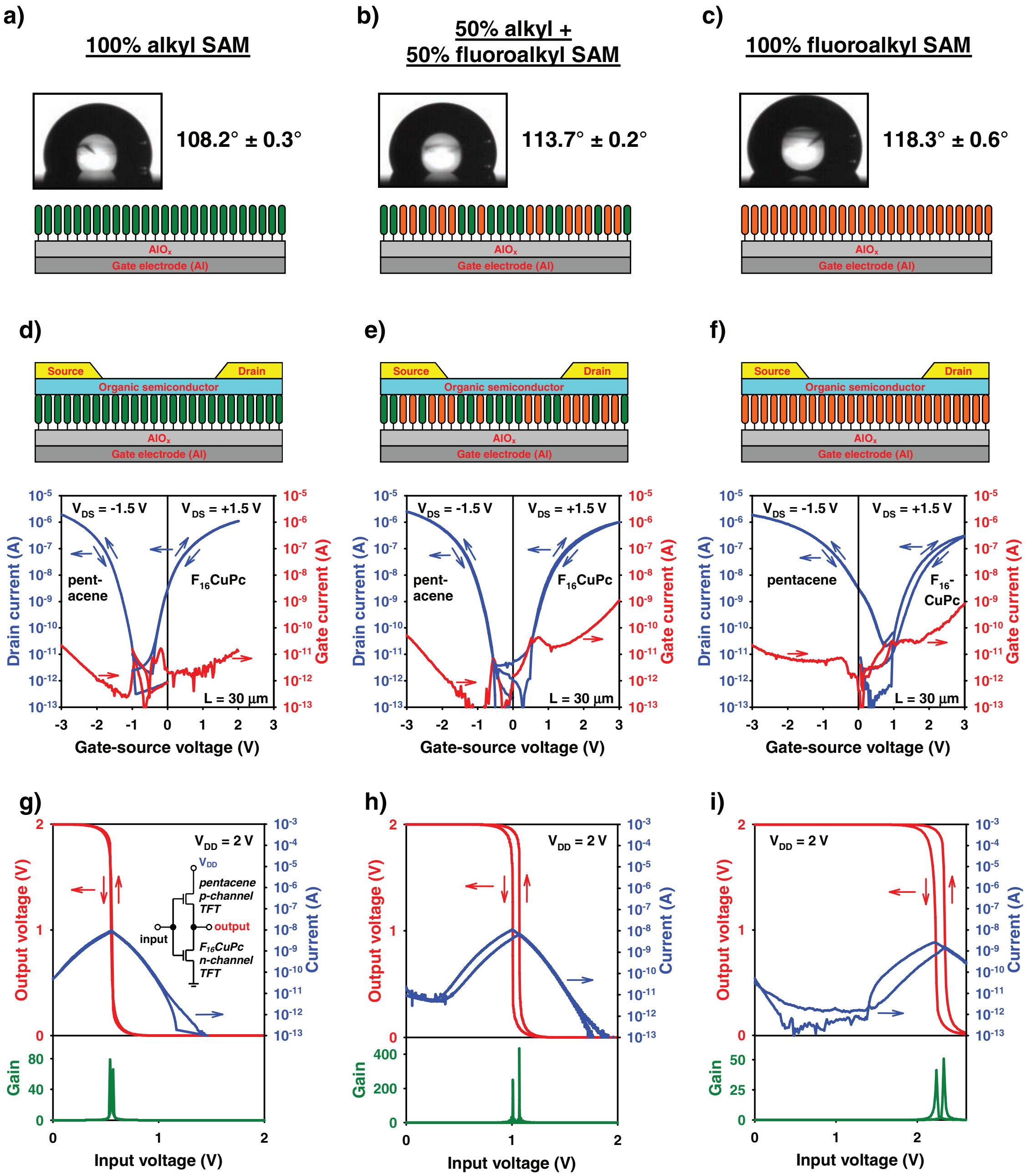

Figure 3. a–c) Water contact angles measured on a self-assembled monolayer (SAM) of 100% alkyl phosphonic acid (a), on a mixed SAM of 50% alkyl and 50% fluoroalkyl phosphonic acid (b), and on a SAM of 100% fluoroalkyl phosphonic acid (c). d–f) Schematic cross-sections and transfer characteristics of pentacene p-channel TFTs and $F_{16}CuPc$ n-channel TFTs with three different SAMs as the gate dielectric: SAM of 100% alkyl phosphonic acid, mixed SAM of 50% alkyl and 50% fluoroalkyl phosphonic acid, and SAM of 100% fluoroalkyl phosphonic acid. g–h) Transfer characteristics of complementary inverters (each composed on one pentacene and one $F_{16}CuPc$ TFT) with the same SAMs. Using the mixed SAM of 50% alkyl and 50% fluoroalkyl phosphonic acid, the inverter has a switching voltage of exactly half the supply voltage (1 V) and a low power consumption of 20 pW (the product of the supply voltage, 2 V, and the maximum supply current, 10 pA).

dielectrics of 100% alkyl, 50% alkyl + 50% fluoroalkyl, and 100% fluoroalkyl SAMs. Due to the small thickness and large capacitance of the AlO_x/SAM gate dielectrics, all transistors operate with low voltages (3 V). The gate currents are no greater than 10^{-9} A, confirming the formation of dense monolayers for all SAM compositions. Atomic force microscopy (AFM) images of the semiconductor films deposited onto the SAMs show no significant differences in film growth depending on the SAM composition (see Figure S4, Supporting Information).

Figure 3 shows that TFTs with 100% alkyl SAM dielectrics have negative threshold voltages (–1.1 V for pentacene TFTs, –0.3 V for $F_{16}CuPc$ TFTs), while TFTs with 100% fluoroalkyl SAM dielectrics have positive threshold voltages (0.5 V for pentacene TFTs, 1.1 V for $F_{16}CuPc$ TFTs). The difference in threshold voltage between 100% alkyl and 100% fluoroalkyl SAMs is about 1.5 V, which is about half the maximum supply voltage. Inside this "window," the threshold voltage can be tuned continuously to any desired value by adjusting the mixing ratio in the adsorption solution. We found that threshold voltages that are symmetric with respect to $V_{GS} = 0$ are obtained for a mixing ratio of 50/50 (see Figure 3e and Figure S5, and Table S1, Supporting Information).

Figure 3g–i show the transfer characteristics of complementary inverters based on the pentacene p–channel and F_{16}CuPc n–channel TFTs from Figure 3d–f. The effect of the SAM composition on the inverter switching voltage is clearly seen. When both TFT threshold voltages are negative (100% alkyl SAM), the inverter switching voltage is very close to the ground potential, so the inverter is very susceptible to electrical noise. When both threshold voltages are positive (100% fluoroalkyl SAM), the switching voltage is actually greater than the supply voltage, so the inverter cannot switch unless the input voltage exceeds the supply voltage. By selecting a mixing ratio that provides symmetric TFT threshold voltages (50% alkyl + 50% fluoroalkyl SAM), an inverter switching voltage of exactly half the supply voltage (1 V) is obtained (see Figure 3h).

One of the benefits of placing the switching voltage at half the supply voltage is greater noise immunity: Even if noise were to cause the input voltage to deviate by close to half the supply voltage in either direction, the inverter would still produce the correct output signal. A circuit's immunity against electrical noise is quantified as the noise margin: The inverter in Figure 3h (50% alkyl + 50% fluoroalkyl SAM) has a noise margin of 0.8 V (80% of ½V_{DD}; see Figure S6, Supporting Information); this is the largest noise margin reported so far for an organic circuit.[22]

A second important benefit of a symmetric switching voltage is that the circuits can be operated with lower supply voltages. This can be seen in **Figure 4** where the signal delay of two complementary ring oscillators is plotted as a function of the supply voltage. The ring oscillator that uses TFTs with a 100% alkyl SAM requires a minimum supply voltage of 1.5 V, while the ring oscillator with the mixed SAM operates with supply voltages as low as 1.0 V, which is the smallest supply voltage reported for organic complementary circuits to date.

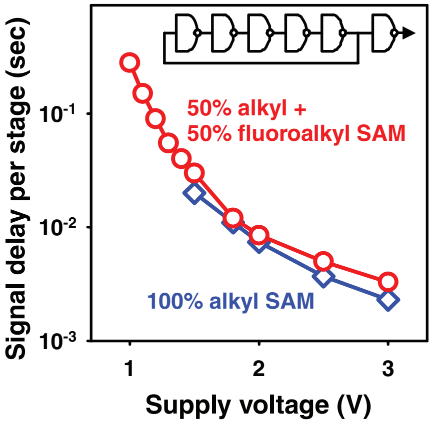

Figure 4. Signal delay per stage as a function of supply voltage for two five–stage organic complementary ring oscillators: One is based on TFTs with a mixed SAM of 50% alkyl and 50% fluoroalkyl phosphonic acid as the gate dielectric (red curve), the other is based on TFTs with a 100% alkyl phosphonic acid SAM dielectric (blue curve). The ring oscillator with the optimized mixed SAM gate dielectric operates with a supply voltage as low as 1 V. All TFTs have a channel length of 20 µm.

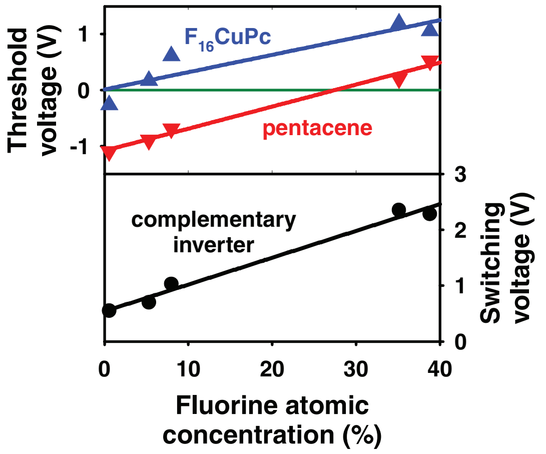

Figure 5. Relationship between the fluorine atomic concentration in the SAM gate dielectric (measured by XPS) and the threshold voltages of the p–channel and n–channel TFTs and the switching voltage of the complementary inverters.

Despite the fact that the relationship between the mixing ratio in solution and the SAM composition is not linear (as reported by Bain et al.[19] and as seen in Figure 2), the exact threshold voltages and switching voltages of TFTs and circuits with mixed SAM dielectrics can nonetheless be accurately predicted after calibration. **Figure 5** shows that the relationship between the threshold voltage and the atomic concentration of fluorine in the SAM-based gate dielectric (as determined by XPS) is indeed linear, as one would expect based on electrostatic considerations. Quantitatively, the change in threshold voltage induced by a change in atomic fluorine concentration is about 40 mV/%. These results demonstrate that ultra-thin dielectrics based on mixed organic monolayers provide a powerful method to continuously tune the threshold voltage of organic transistors in a deterministic and reproducible manner.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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